

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 7/04	A1	(11) International Publication Number: WO 95/06019 (43) International Publication Date: 2 March 1995 (02.03.95)
(21) International Application Number: PCT/US94/09435 (22) International Filing Date: 22 August 1994 (22.08.94) (30) Priority Data: 08/111,222 23 August 1993 (23.08.93) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventors: CHEN, Catherine, S., H.; 102 Pinegrove Road, Berkley Heights, NJ 07922 (US). WENTWEK, Steven, E.; 19 Harwin Drive, East Brunswick, NJ 08816 (US). (74) Agents: SINNOTT, Jessica, M. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		(81) Designated States: AU, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ISOLATION OF HIGH PURITY DIAMONDROID, FRACTIONS AND COMPONENTS (57) Abstract A method of separating high purity diamondroid fractions from a mixture of diamondroid compounds comprising the steps of: (a) providing a feed containing at least 25 weight percent diamondroid compounds and at least 40 total weight percent substituted and unsubstituted adamantane, at least 30 total weight percent substituted and unsubstituted diamantane, and at least about 5 total weight percent substituted and unsubstituted triamantane; (b) distilling an overhead fraction in the absence of a reflux; (c) cooling said overhead to a temperature above the freeze point of the feed mixture; (d) recovering unsubstituted diamondroid solids from said overhead fraction at a purity of at least 90 weight percent, and (e) distilling said overhead fraction with reflux to recover substituted diamondroids.		

THIS PAGE BLANK (USPTO)

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C07C 7/04	A1	(11) International Publication Number: WO 95/06019 (43) International Publication Date: 2 March 1995 (02.03.95)
(21) International Application Number: PCT/US94/09435 (22) International Filing Date: 22 August 1994 (22.08.94) (30) Priority Data: 08/111,222 23 August 1993 (23.08.93) US (71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US). (72) Inventors: CHEN, Catherine, S., H.; 102 Pinegrove Road, Berkley Heights, NJ 07922 (US). WENTWEK, Steven, E.; 19 Harwin Drive, East Brunswick, NJ 08816 (US). (74) Agents: SINNOTT, Jessica, M. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).		(81) Designated States: AU, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ISOLATION OF HIGH PURITY DIAMONDOID, FRACTIONS AND COMPONENTS (57) Abstract A method of separating high purity diamondoid fractions from a mixture of diamondoid compounds comprising the steps of: (a) providing a feed containing at least 25 weight percent diamondoid compounds and at least 40 total weight percent substituted and unsubstituted adamantane, at least 30 total weight percent substituted and unsubstituted diamantane, and at least about 5 total weight percent substituted and unsubstituted triamantane; (b) distilling an overhead fraction in the absence of a reflux; (c) cooling said overhead to a temperature above the freeze point of the feed mixture; (d) recovering unsubstituted diamondoid solids from said overhead fraction at a purity of at least 90 weight percent, and (e) distilling said overhead fraction with reflux to recover substituted diamondoids.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

ISOLATION OF HIGH PURITY DIAMONDROID FRACTIONS AND COMPONENTS

The present invention relates to a method for recovering high purity diamondoid fractions and components from a mixture containing substituted and unsubstituted diamondoid compounds.

5 Many hydrocarbonaceous mineral streams contain some small proportion of diamondoid compounds. These high boiling, saturated, three-dimensional polycyclic organics are illustrated by adamantane, diamantane, triamantane and various side chain substituted homologues,
10 particularly the methyl derivatives. These compounds have high melting points and high vapor pressures for their molecular weights and have recently been found to cause problems during production and refining of hydrocarbonaceous minerals, particularly natural gas, by
15 condensing out and solidifying, thereby clogging pipes and other pieces of equipment. For a survey of the chemistry of diamondoid compounds, see Fort, Jr., Raymond C., The Chemistry of Diamond Molecules, Marcel Dekker, 1976, as well as U.S. Patents 5,019,660 to Chapman and
20 Whitehurst and 5,053,434 to Chapman.

In recent times, new sources of hydrocarbon minerals have been brought into production which, for some unknown reason, have substantially larger concentrations of diamondoid compounds. Some of these diamondoid mixtures
25 cause severe plugging problems in downstream processing equipment. Other diamondoid mixtures remain in the liquid phase under natural gas processing conditions and can be easily removed in a liquid knockout drum.

The problem of diamondoid deposition and plugging in
30 natural gas production equipment has been successfully addressed by a controlled solvent injection process. U.S. Patent 4,952,748 to Alexander and Knight teaches the process for extracting diamondoid compounds from a hydrocarbon gas stream by contacting the diamondoid-laden
35 hydrocarbon gas with a suitable solvent to preferentially

-2-

dissolve the diamondoid compounds into the solvent. U.S. Patent 5,016,712 to Cullick and Roach teaches a method for locating the solvent injection point within the natural gas wellbore.

5 Further studies have revealed that separating diamondoid compounds into high purity fractions is complicated by their overlapping boiling points and relatively high vapor pressures. U.S. Patents 4,952,747, 4,952,749, and 4,982,049 to Alexander et al. teach
10 various methods of concentrating diamondoid compounds which dissolved in a solvent for, among other reasons, recycling the lean solvent fraction for reuse, and each of these processes produces an enriched solvent stream containing a mixture of diamondoid compounds. While
15 these techniques meet the industrial need for a constant supply of relatively lean solvent for continuous recycle, the diamondoid-enriched streams rejected by these processes are not sufficiently pure to themselves be commercially useful. As mentioned above, conventional
20 distillation of diamondoid-containing solvent mixtures is complicated by the fact that diamondoid compounds exhibit vapor pressures which are unusually high for their molecular weights.

25 U.S. Patent 5,120,899 to Chen and Wentzek, which is incorporated by reference as if set forth at length herein, teaches a method of recovering the total diamondoid mixture without contamination using a high boiling point solvent which is injected into the natural gas wellbore.

30 Thus it would be desirable to provide a method for separating these recovered diamondoid mixtures into high purity fractions and components.

35 This invention provides a method for separating high purity diamondoid fractions and components from a mixture of alkylated and non-alkylated diamondoid compounds. The steps of this invention are both counterintuitive and highly effective for separating high purity, high

-3-

melting, unsubstituted diamondoids such as adamantane, diamantane, and triamantane from a complex mixture of substituted diamondoids.

5 In addition, removing higher melting fractions from the diamondoid mixture useful as a feedstock in this invention naturally lowers the freeze point of the resulting mixture, rendering the mixture more desirable as a component in a fuel or lubricant. The term "freeze point" as used herein refers to the highest temperature
10 at which the liquid mixture precipitates solids from the mixture. Freeze point behavior has been studied extensively, particularly in the fields of jet and rocket engine fuels. In these applications, it is generally accepted that blending in a lower molecular weight
15 solvent such as hexanes or heptanes will effectively lower the freeze point. Removing lower boiling fractions from the feedstock useful in the present invention, on the other hand, surprisingly causes no substantial increase in the freeze point, also has been found to
20 beneficially depress the freeze point. This behavior runs counter to the industry practice of blending lighter fractions with heavier fractions to lower the freeze point of the resulting mixture. Further, the lower boiling components are useful as specialty chemicals and
25 as feedstocks for pharmaceuticals.

The method of the invention comprises the steps of

- 30 (a) providing a feed mixture of diamondoid compounds containing at least about 40 total weight percent substituted and unsubstituted adamantane, at least about 30 total weight percent substituted and unsubstituted diamantane, and at least about 5 total weight percent substituted and unsubstituted triamantane;
- 35 (b) distilling an overhead fraction from said feed mixture of diamondoid compounds, said overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, and

-4-

having a freeze point which is higher than the freeze point of said feed mixture;

(c) cooling said overhead fraction to a temperature above the freeze point of said feed mixture; and

5

(d) recovering unsubstituted diamondoid solids from said overhead fraction at a purity of at least about 90 weight percent.

10

In a preferred embodiment, the method further comprises recrystallizing the unsubstituted diamondoid solids obtained in the recovery step (d) in a suitable solvent such as hexanes or heptanes to a purity of at least about 99 weight percent.

15

The invention provides, in a second aspect, a method for separating high purity diamondoid fractions from a mixture of diamondoid compounds comprising the steps of:

(a) providing a feed mixture of diamondoid compounds containing unsubstituted adamantane, unsubstituted diamantane, unsubstituted triamantane, and substituted diamondoid compounds;

20

(b) distilling a first overhead fraction from said feed mixture, said first overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said first overhead fraction is further characterized by a higher freeze point than said feed mixture;

25

(c) cooling said first overhead fraction to recover unsubstituted adamantane from said cooled first overhead fraction in purity of at least about 90 weight percent;

30

(d) continuing said distillation to provide a second overhead fraction which upon cooling becomes a liquid and contains predominately a mixture of substituted adamantanes with each component having a higher carbon number than the unsubstituted adamantane and the mixture having a substantially lower freezing point than unsubstituted adamantane;

35

(e) distilling said feed mixture to provide a third overhead fraction, said third overhead fraction

-5-

characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said third overhead fraction is further characterized by a higher freeze point than said feed mixture;

(f) cooling said third overhead fraction to recover unsubstituted diamantane from said cooled second overhead fraction in purity of at least about 90 weight percent;

(g) continuing said distillation to provide a fourth overhead fraction which upon cooling becomes a liquid and contains predominately a mixture of substituted diamantanes with each component of said mixture of substituted diamantanes having a higher carbon number than the unsubstituted diamantane and said mixture of substituted diamantanes having a substantially lower freezing point than unsubstituted diamantane;

(h) distilling a fifth fraction from said feed mixture, said fifth overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said fifth overhead fraction is further characterized by a higher freeze point than said feed mixture; and

(i) cooling said fifth overhead fraction to recover unsubstituted triamantane from said cooled fifth overhead stream in purity of at least about 90 weight percent; and

(j) recovering pot material containing a major amount of substituted triamantane and minor amounts of tetramantane and pentamantane.

In a preferred embodiment, the recovered pot material is percolated through a sorbent such as activated alumina or activated carbon to remove impurities such as color bodies and other polar compounds.

The diamondoid mixtures useful as feedstocks in the present invention may be solid, liquid, or a mixture of solid and liquid under ambient conditions, and useful feedstocks for the present process must contain at least

-6-

some liquid. If the feedstock contains solids, it may optionally be filtered before the distillation stage, although this is not required. If the feedstock contains more than about 25 weight percent of diamondoid compounds which are normally solid under ambient conditions, the method of the invention preferably comprises an additional short-path distillation step in the absence of reflux, or filtration at ambient temperature to remove solids. For a general description of short-path distillation, see U.S. Patent 5,120,899 to Chen and Wentzek, which is incorporated by reference as if set forth at length herein. If the feedstock contains less than about 25 weight percent of diamondoid compounds which are normally solid under ambient conditions, then the method may be carried out in a multistage distillation apparatus without the optional short-path distillation or filtration steps.

The method of the invention requires no additional concentration of the diamondoid fractions to precipitate the unsubstituted diamondoid solids.

Figure 1 is a gas chromatograph (capillary column) of a normally liquid mixture of diamondoid compounds including substituted adamantanes, unsubstituted adamantane, substituted diamantanes, unsubstituted diamantane, and triamantane.

Figure 2 is a gas chromatograph (capillary column) of a mixture of diamondoid compounds which contains both liquid and crystalline solids under ambient conditions.

Figure 3a is a gas chromatograph (capillary column) of the adamantanes fraction (including both substituted adamantanes and unsubstituted adamantane) of the normally liquid mixture of diamondoid compounds represented by the gas chromatograph of Figure 1.

Figure 3b is a gas chromatograph (capillary column) of adamantane in heptane. The adamantane was separated from the normally liquid mixture of diamondoid compounds

-7-

represented by the gas chromatograph of Figure 1 by the process of the present invention.

Figure 4a is a gas chromatograph (capillary column) of the diamantanes fraction (including both substituted
5 diamantanes and unsubstituted diamantane) of the normally liquid mixture of diamondoid compounds represented by the gas chromatograph of Figure 1.

Figure 4b is a gas chromatograph (capillary column) of diamantane in heptane. The diamantane was separated
10 from the normally liquid mixture of diamondoid compounds represented by the gas chromatograph of Figure 1 by the process of the present invention.

Figure 5a is a gas chromatograph (capillary column) of the triamantanes and tetramantanes fraction (including
15 both substituted and unsubstituted triamantanes and tetramantanes) of the normally liquid mixture of diamondoid compounds represented by the gas chromatograph of Figure 1.

Figure 5b is a gas chromatograph (capillary column) of triamantane in heptane. The triamantane was separated
20 from the normally liquid mixture of diamondoid compounds represented by the gas chromatograph of Figure 1 by the process of the present invention.

Feedstocks

The feedstock composition is a critical aspect of the present invention. The feedstock must contain at least one unsubstituted diamondoid compound selected from the group consisting of adamantane, diamantane, and triamantane, together with one or more alkyl-substituted diamondoid compounds. Figure 1 shows a gas chromatograph of a normally liquid mixture of diamondoid compounds useful as a feedstock in the present invention, which mixture includes unsubstituted adamantane, substituted adamantanes, unsubstituted diamantane, substituted diamantanes, unsubstituted triamantane, substituted triamantane, as well as tetramantanes and pentamantanes in minor quantities.

The preferred processing steps in the method of the invention depend upon the content of normally solid diamondoid compounds in the feedstock. If the feedstock contains more than about 25 weight percent of diamondoid compounds which are normally solid under ambient conditions, the method of the invention preferably comprises an additional short-path distillation step in the absence of reflux, or filtration at ambient temperature to remove solids. If the feedstock contains less than about 25 weight percent of diamondoid compounds which are normally solid under ambient conditions, then the method may be carried out in a multistage distillation apparatus without the optional short-path distillation or filtration steps. Examples of feedstocks which are preferably filtered at ambient or lower temperature or which are preferably distilled in a short-path distillation apparatus prior to multistage distillation are shown below in Examples 8 and 9.

Fractional Separation

The present invention may be carried out (a) in a short path distillation apparatus without reflux followed by (b) a multiple stage distillation apparatus, if the feed mixture contains a large amount (i.e. 25 wt% or more) of unsubstituted diamondoids. If the feed contains less than about 25 wt% unsubstituted diamondoids, the invention may be carried out without the initial short-path distillation step.

The diamondoid-containing feed may suitably be charged to a distillation vessel under vacuum conditions ranging from about 0.05 to about 25 Torr, preferably from about 0.1 to about 10 Torr, most preferably from about 0.2 to about 2 Torr. The distillation is appropriately conducted in a vessel rated for full vacuum service under the operating temperature selected from the range of about 0°C to about 150°C. The distillation vessel useful for the optional short-path distillation step is preferably connected to a receiver by heated lines of relatively large diameter to avoid condensation or sublimation of valuable products before the products reach the receiver. The separation steps of the present invention may be conducted in batch or continuous mode.

The distillation vessel useful for the optional short-path distillation step may, for industrial applications, more particularly comprise a flash drum rated for full vacuum service at the feedstock endpoint temperature. In one laboratory embodiment, the short-path distillation/crystallization stage may be conducted in a Kugelrohr apparatus as described below in the Examples. For example, a vessel equipped with suitable heating means, such as external or internal steam or electric heating coils and a temperature controller would be a useful distillation vessel. The vessel preferred for industrial applications of the multistage distillation of the invention contains one or more sections of distillation trays or packing.

-10-

To initiate the separation process step in the preferred batch mode, the distillation vessel is filled with diamondoid-containing feed and the temperature is raised incrementally and pressure is decreased until a vapor product flow is detected, at which point the temperature and pressure are held constant until the vapor product flow ceases. The pot temperature is then raised and/or the pressure is decreased to continue separation.

The distillation step of the invention produces at least two fractions which are enriched in diamondoid compounds having a single backbone structure. As used herein, the term "backbone structure" refers to the structure of the unsubstituted diamondoid homologs, which include adamantane, diamantane, triamantane, tetramantane, and pentamantane. Thus adamantane and any adamantane derivative which can be made by substituting a functional group (or groups) for at least one hydrogen of the unsubstituted adamantane share a single backbone structure. Examples of substituent groups include alkyl, aryl, and halogens, merely to name a few. For example, a fraction enriched in diamondoid compounds having the backbone structure of adamantane would contain a major portion of adamantane and various alkyl substituted adamantanes, such as methyl- and ethyl-substituted adamantanes. On the other hand, a fraction enriched in diamondoid compounds having the backbone structure of diamantane would contain a major portion of diamantane and various substituted diamantanes, for example, alkyl-substituted diamantanes such as the methyl- and ethyl-substituted diamantanes.

Surprisingly, it has been found that crystalline solids of substantially pure adamantane, diamantane, or triamantane were readily obtained in overhead fractions prior to substituted adamantane, diamantane, or triamantane, respectively. After these solids are collected from the cooled overhead stream, the liquid

-11-

portions of the diamondoid fractions may be optionally be further purified by repeating the distillation and sublimation steps of the invention. The liquids may be distilled individually or may be recombined before charging the mixture to the distillation/sublimation stage of the invention.

In a preferred embodiment, this invention separates a mixture of substituted and unsubstituted diamondoids into at least one liquid fraction and one solid fraction, and typically produces about three liquid fractions and three solid fractions. The solids produced by the distillation/ sublimation stages are of unusually high purity, typically exceeding 90 to 95 weight percent purity.

For feedstocks containing less than about 25 weight percent diamondoid compounds which are normally solid under ambient conditions, the method of the invention is preferably conducted in a suitable multi-stage distillation tower. Tower temperature must be carefully controlled to avoid sublimation of solids in the upper tower and overhead conduit. The temperatures in the overhead condenser and reflux lines must be carefully controlled to avoid plugging the conduit with crystalline materials. One example of a multi-stage distillation tower useful in the distillation/sublimation stage of the invention is an ASTM D-2887 distillation unit as described below in Example I with the addition of supplemental temperature controllers in the upper tower sections and overhead conduit to avoid plugging.

Table 1, below, illustrates three diamondoid mixture useful as feedstocks in the present invention. Mixture A contains adamantanes, diamantanes, and triamantanes. Mixture B contains diamantanes and triamantanes. Mixture C contains adamantanes with trace amounts of higher molecular weight diamondoids.

-12-

Table 1
Examples of Useful
Diamondoid-Containing Feedstocks (wt.%)

	A	B	C
Compounds *			
adamantane	1.364	none	1.234
1-methyl adamantane	5.615	none	7.617
1,3-dimethyl adamantane	6.070	none	10.174
1,3,5-trimethyl adamantane	2.438	none	4.796
1,3,5,7-tetraamethyl adamantane	0.413	none	0.713
2-methyl adamantane	1.003	none	1.754
t-1,4-Dimethyl adamantane	1.514	none	2.980
c-1,4-Dimethyl adamantane	1.516	none	3.459
1,3,6-Trimethyl adamantane	1.774	none	4.083
1,2-Dimethyl adamantane	1.483		3.368
1r, 3,4t-Trimethyl adamantane	2.056		4.647
1r, 3,4c-Trimethyl adamantane	2.117		4.898
1,3,5,6-tetramethyl adamantane	2.044		5.308
1-ethyl adamantane	0.630		1.523
2,6-; 2e,4e-; 2e,4a-diMe Ad	0.118		0.285
1,2,3,5-tetramethyl	0.07		0.17
1-ethyl-3-methyl adamantane	2.16		5.17
1,2,3-Trimethyl adamantane	0.34		0.81
1-ethyl-3,5-dimethyl adamantane	1.582	0.012	3.909
1-ethyl-3,5,7-trimethyl adamantane	0.424		1.031
1,2,3,5,7-pentamethyl adamantane	1.050	0.029	2.489
Other adamantanes	14.432	6.631	23.083
Total adamantanes	50.213	6.672	93.501
Diamantane	3.967	5.560	1.342
4-Methyl-diamantane	5.345	8.338	1.522
4,9-Dimethyl-diamantane	1.710	2.784	0.400
1-Methyl-diamantane	3.343	5.664	0.624

-13-

	A	B	C
Compounds *			
2,4-Dimethyl-diamantane	2.078	3.611	0.395
1,4-dimethyl diamantane	2.563	4.509	0.406
1,4,9-trimethyl diamantane	1.103	1.981	0.196
3-methyl diamantane	2.384	4.241	0.359
4,8-Dimethyl diamantane	1.618	2.970	0.195
4-Ethyl-diamantane	0.584	1.206	0.043
Other diamantanes	16.597	34.282	1.017
Total diamantanes	41.292	75.146	6.499
Triamantane	1.175	2.608	0.017
9-methyl triamantane	1.151	2.583	0.016
9,15-dimethyl triamantane	0.233	0.521	
3-Me & 3,9-diMe triamantanes	0.696	1.560	
7,9-diMe & 3,9,15-triMe triamantanes	0.489	1.136	
4-Me & 4,9,15-triMe triamantanes	0.440	0.973	
4,9- & 6,9-dimethyl triamantanes	0.184	0.419	
5-methyl triamantane	0.289	0.661	
5,9-methyl triamantane	0.180	0.395	
8-Me & 5,9,15-triMe triamantanes	0.244	0.585	
9,14-dimethyl triamantanes	0.144	0.238	
8,9-dimethyl triamantanes	0.069	0.210	
16-methyl-, a diMe- & a triMe-triamantanes	0.366	0.837	
2-methyl triamantane	0.118	0.302	
other triamantanes	1.857	4.402	

	A	B	C
Compounds *			
Total triamantanes + methyl and dimethyl derivatives	7.605	17.430	0.033
iso-tetramantane + A + B	0.119	0.283	
anti-tetramantane	0.023	0.059	
other tetramantanes	0.139	0.410	
Total tetramantane	0.281	0.752	0.000

1 This sample contained 6.821 % of lower boiling materials.

10 * Prefixes a-, e-, c-, and t- refer to axial, equatorial, cis-, and trans- relationship of substituents in the same cyclohexane ring bearing the substituents in the diamondoids.

EXAMPLE 1

15 A distillation was carried out in a ASTM D-2887 distillation unit having a column packed with stainless steel saddles. A two-neck flask was used to allow a flow of nitrogen stream through the material to be distilled. Two thousand grams of a crude diamondoid mixture (represented by the gas chromatograph of Figure 1) was
20 percolated through activated alumina and charged into the flask. Nitrogen was passed through the material at the beginning of the distillation at 20 CC/Min. It was observed that by simply bubbling nitrogen through the bottom of the liquid, even at room temperature, some low
25 boiling point material was collected in a dry ice/acetone trap. This low boiling point material was not characterized by diamondoid structure. The remainder of the low boiling point material was collected in the receiver. The combined materials from the dry
30 ice/acetone trap and the receiver constituted the low-boiling pre-adamantane fraction which was co-produced with the diamondoids. After the first fraction, the nitrogen flow was increased to 60 CC/Min. Table 2 summarizes the distillation results.

-15-

After the distillation, fractions 5, 6, 7, 8, and 9 were combined. Fractions 10 and 11 were combined and saved for further distillation with similar mixtures from additional distillations.

5EXAMPLE 2

This example illustrates the method of obtaining the fraction containing triamantanes and tetramantanes. Distillation residue accumulated from five similar distillations as described in Example 1 (1789 grams) was charged to the same distillation unit as described in Example 1. The mixture contained 3.2% adamantanes, 62.3% diamantanes, 34.5% triamantanes + tetramantanes. The distillation of this mixture to separate the adamantanes and diamantanes from the triamantanes and tetramantanes is described in Table 3.

1015

TABLE 2
Distillation of Normally Liquid Diamondoids: Mixture Conditions And Products

Fr.	Reflux Ratio	Head, °C	Column, Bottom	Top, °C	Pot, °C	mmHg	Pre-Ad	Ad	Di	Tri-Tetra	Wt., gm
5	1.	8:1	23-24	28-29	23-24	140-190	99	1	0	0	114.0
	2.	8:1	42	68	210	atm.	13.1	86.9	0	0	19.1
	3.	8:1	186	222	215	atm.	33.2	66.8	0	0	4.5
	4.	8:1	193	225	216	atm.	16.3	83.1	0	0	13.3
10	(Adamantane crystals condensed at the top of condenser and take-off arm. The solid was melted and collected. Pure adamantane was obtained by recrystallization from heptane.)										
	5.	8:1	140	231	217	249	atm.	1.5	98.5	0	207.0
	6.	8:1	144	232	218	249	atm.	0.1	99.1	0.8	192.8
15	(cooled down the system. Started vacuum distillation.)										
	7.	8:1	39	100	98	100	0.3	0	100	0	113.7
	8.	8:1	42	100	100	100	0.3	0	99.7	0.3	34.5
	9.	25:1	58	119	114	119	0.3	0	97.6	2.4	292.4
20	(Diamantane crystals condensed at the top of condenser and take-off arm. The solid was melted and collected. Pure diamantane was obtained by recrystallization from heptane.)										
	10.	25:1	67	130	125	139	0.25	0	57.9	42.1	31.6
	11.	25:1	74	137	130	140	0.15	0	35.2	64.8	85.4
	12.	25:1	89	156	150	160	0.35	0	0.6	96.8	462.6

(The pot material, containing diamantanes, triamantanes and tetramantanes, was collected to be combined with similar pot materials from additional distillations to further separate the diamantanes from the triamantanes and tetramantanes as described in Example II.)

-17-

TABLE 3
Isolation of Triamantanes - Tetramantanes Fraction and Triamantane Component

Fr.	Reflux Ratio	Head, °C	Column, Bottom	°C Top	Pot °C	mmHg	Ad	Prod. Composition, % Di	Tri+Tetra	Wt., gm
(The mixture was under total reflux at 0.5 mm Hg and 125 C pot temperature for 12.5 hours.)										
1.	3:1	59	101	97	124	0.5	97.4	2.6	0	18.6
2.	3:1	78	113	110	138	0.5	90.8	9.2	0	13.8
(Solid diamantane was collected.)										
3.	3:1	82	123	118	137	0.5	9.7	90.3	0	38.3
4.	3:1	89	124	120	138	0.5	4.4	95.6	0	141.2
5.	6:1	83	128	120	145	0.4	3.8	96.2	0	275.2
6.	8:1	91	111	108	154	0.5	2.3	97.7	0	324.6
7.	8:1	100	111	108	168	0.5	0	99.9	0.1	236.3
8.	8:1	91	111	107	164	0.35	0	99.6	0.4	69.3
9.	8:1	93	106	107	167	0.35	0	80.5	13.7	44.4

(Triamantane crystals were collected at the take-off, and subsequently purified by recrystallization from heptane.)

10. ----Pot material----
 (The pot material was yellowish and viscous, 8.09 CS at 100 C. The material was then treated with a mixture of activated alumina (97%) and charcoal (3%). The activated alumina/charcoal treatment produced a virtually colorless product.)

20

-18-

EXAMPLES 3 AND 4

Examples 3 and 4 illustrate separation and isolation procedures of diamondoids containing high percentage of solids.

5EXAMPLE 3

A diamondoid mixture was recovered from a natural gas field according to the procedure taught in U.S. Patent 5,120,899 to Chen and Wentzek. The diamondoid mixture contained ~10% solid material at room temperature. The solid material, after recrystallization from heptane, was identified to be pure diamantane.

10

Distillation of the sample diamondoid mixture was attempted three times in the ASTM D-2887 distillation unit described above. Adamantane sublimed even at room temperature under a vacuum of ~1mm Hg. Adamantane was followed by liquid alkyl substituted adamantanes. However, when the diamantane started to sublime, the take-off, the condenser (although jacketed by hot ethylene glycol), and the pathway to the receiver were plugged firmly with diamantane. Unlike the condensed adamantane, the diamantane could not be unplugged by using a heat gun, therefore, the distillation had to be stopped. The diamantane was removed by disassembling the unit and washing the clogged parts with hot heptane.

152025EXAMPLE 4

In Example 4, the diamondoid mixture of Example 3 was separated first by short-path distillation to the adamantanes, diamantanes + triamantanes; followed by isolation of crystalline adamantane and diamantane from each fraction; then followed by distillation of the remainder liquid as described in Examples 1 and 2. Triamantane was isolated at the end of the distillation as described in Example 2.

30

-19-

EXAMPLE 5

Example 5 demonstrates short-path distillation in a Kugelrohr apparatus. A solids-containing diamondoid mixture (1135 gm) was charged into the distillation pot of a 3-liter Kugelrohr apparatus. The receiver was cooled in a Dry ice/acetone mixture. A vacuum of 0.7 mm Hg was applied. While the apparatus was rotated the pot was heated to 30°C. After 5.5 hours, 649.7 gm of material had been collected in the receiver, and 484.2 gm material remained in the pot. The material in the receiver contained 99% adamantanes and 1% diamantanes. The pot material contained 90% diamantanes + triamantanes and 10% adamantanes.

EXAMPLE 6

The fraction of adamantanes recovered in Example 5 contained a small amount of solids. It was charged into a sublimator, or a distillation unit which was equipped with a large-bore take-off. At a pot temperature of 89°C and a vacuum of 11.6 mm Hg solid adamantane was obtained as the product. The solid adamantane was followed by clear liquid adamantanes if the distillation was continued. The adamantane was further purified by recrystallization from heptane.

The fraction of diamantanes obtained in Example 5 contained a large amount of solids (bottom 1/3 of the material). The solids were separated by filtration. After recrystallization from heptane, the solids were identified to be pure diamantane. The filtrate was combined with the liquid from the adamantanes and/or from other short-path distillations for further separation by distillation.

EXAMPLE 7

The liquid diamondoids were combined and distilled as described in Examples 1 and 2. The conditions were similar to those described. The product distillate was continuously monitored during the distillation by GC analysis to obtain clean-cut fractions. Fractions of

-20-

similar compositions were combined after the distillation. Additional smaller amounts of adamantane and diamantane were isolated during the distillation. Triamantane was isolated and recrystallized as described in Example 2.

Examples 8-10

Examples 8-10 illustrate diamondoid feedstocks useful in the present invention. Examples 8 and 9 contain more than 50 weight percent of diamondoid compounds which are typically solid under ambient conditions. The feedstocks of Examples 8 and 9 are preferably first purified in the short-path distillation step of the invention, prior to the multistage distillation steps of the invention. Alternatively, feedstocks such as those described in Examples 8 and 9 may be filtered at ambient or lower temperature to remove solids.

Example 10 illustrates a diamondoid feedstock containing less than about 25 weight percent of diamondoids which are typically solid under ambient conditions. The solids content of the feedstock shown in

-21-

Example 10 is low enough that the optional short-path distillation step is not required.

Table 4
Comparison of Sample Diamondoid Feedstocks

Example No.	8	9	10	
Component	Composition, Weight Percent			
Adamantane	17.08	13.24	2.96	*
1-Methyladamantane	26.54	22.77	11.43	*
1,3-Dimethyladamantane	16.40	13.61	12.00	
1,3,5-Trimethyladamantane	3.51	3.02	4.46	
Other Adamantanes	3.21	4.69	47.87	
Diamantane	16.17	15.71	2.27	*
4-Methyldiamantane	7.03	8.53	2.17	
1-Methyldiamantane	2.65	1.25	0.81	
Other Diamantanes	3.06	12.17	77.13	
Triamantane	2.74	2.73	0.98	*
9-Methyltriamantane	1.31	1.60	1.22	*
Other Triamantanes	0.30	0.68	2.67	*
Total solids and likely solids under ambient conditions	63.84	56.73	21.53	

* Typically solid under ambient conditions.

Example 3, above, describes the distillation of a sample diamondoid mixture which was recovered from a natural gas well. The sample diamondoid mixture of Example 3 contained about 10 weight percent of diamondoid compounds which were solid at room temperature. Conventional distillations (ASTM 2887) were also attempted with other mixed diamondoid feedstocks including those feedstocks shown in Examples 8-10. No mixed diamondoid feedstocks which contained at least 25 weight percent of diamondoid compounds which were normally solid at room temperature were found which could be distilled in a conventional (ASTM 29887) distillation

apparatus. Distilling these mixed diamondoid feedstocks (which contained at least about 25 weight percent of diamondoid compounds which were normally solid at room temperature) caused severe plugging of the take-off and condenser early in the distillation procedure.

With the research objective of distilling diamondoid mixtures containing at least about 25 weight percent solids, various process and equipment modifications to overcome the problems of severe plugging in the take-off and condenser were attempted. The attempted process and equipment modifications were unsuccessful and the problem of severe plugging in the take-off and condenser persisted.

An attempt to distill a mixture containing more than about 25 weight percent of diamondoids which are normally solid at room temperature was made. Example 5 is a short-path distillation procedure conducted in a Kugelrohr apparatus. This short-path distillation had no observable reflux. After obtaining fractions enriched in adamantanes, diamantanes, and triamantanes, respectively, these fractions were cooled to room temperature and the precipitated solids were collected. The adamantane, diamantane, and triamantane solids collected from each of the fractions were more than 90 percent pure.

-23-

What is claimed is:

1. A method for separating high purity diamondoid fractions from a mixture of diamondoid compounds comprising the steps of:

5 (a) providing a feed mixture of diamondoid compounds which contains at least 25 weight percent of diamondoid compounds which are normally solid under ambient conditions and which feed mixture further comprises at least about 40 total weight percent
10 substituted and unsubstituted adamantane, at least about 30 total weight percent substituted and unsubstituted diamantane, and at least about 5 total weight percent substituted and unsubstituted triamantane;

15 (b) distilling an overhead fraction from said feed mixture of diamondoid compounds in the absence of reflux such that the freeze point of said overhead fraction is higher than the freeze point of said feed mixture;

(c) cooling said overhead fraction to a temperature above the freeze point of said feed mixture;

20 (d) recovering unsubstituted diamondoid solids from said overhead fraction at a purity of at least about 90 weight percent; and

(e) distilling said overhead fraction of step (d) with reflux to recover substituted diamondoids.

25 2. The method of claim 1 wherein said feed mixture contains less than about 25 weight percent of diamondoid compounds which are solid under ambient conditions.

30 3. The method of claim 1 wherein said feed mixture contains at least about 25 weight percent of diamondoid compounds and wherein said method further comprises at least one distillation step in the absence of reflux.

35 4. The method of claim 1 wherein said feed mixture contains at least about 25 weight percent of diamondoid compounds and wherein said method further comprises at least one filtration step at temperature less than or equal to ambient.

-24-

5. A method for separating high purity diamondoid fractions from a mixture of diamondoid compounds comprising the steps of:

5 (a) providing a feed mixture of diamondoid compounds which contains at least 25 weight percent of diamondoid compounds which are normally solid under ambient conditions and which feed mixture further comprises unsubstituted adamantane, unsubstituted diamantane, unsubstituted triamantane, and substituted diamondoid compounds;

10 (b) distilling a first overhead fraction from said feed mixture in the absence of reflux, said first overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said first overhead fraction is further characterized by a higher freeze point than said feed mixture;

15 (c) cooling said first overhead fraction to recover unsubstituted adamantane from said cooled first overhead fraction in purity of at least about 90 weight percent;

20 (d) continuing said distillation in the absence of reflux to provide a second overhead fraction which upon cooling becomes a liquid and contains predominately a mixture of substituted adamantanes with each component having a higher carbon number than the unsubstituted adamantane and the mixture having a substantially lower freezing point than unsubstituted adamantane;

25 (e) distilling said feed mixture in the absence of reflux to provide a third overhead fraction, said third overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said third overhead fraction is further characterized by a higher freeze point than said feed mixture;

30 (f) cooling said third overhead fraction to recover unsubstituted diamantane from said cooled third overhead fraction in purity of at least about 90 weight percent;

-25-

(g) continuing said distillation in the absence of reflux to provide a fourth overhead fraction which upon cooling becomes a liquid and contains predominately a mixture of substituted diamantanes with each component of said mixture of substituted diamantanes having a higher carbon number than the unsubstituted diamantane and said mixture of substituted diamantanes having a substantially lower freezing point than unsubstituted diamantane;

(h) distilling a fifth fraction from said feed mixture in the absence of reflux, said fifth overhead fraction characterized by an average carbon number which is lower than the average carbon number of said feed mixture, wherein said fifth overhead fraction is further characterized by a higher freeze point than said feed mixture;

(i) cooling said fifth overhead fraction to recover unsubstituted triamantane from said cooled fifth overhead stream in purity of at least about 90 weight percent;

(j) recovering pot material containing a major amount of substituted triamantane and minor amounts of tetramantane and pentamantane; and

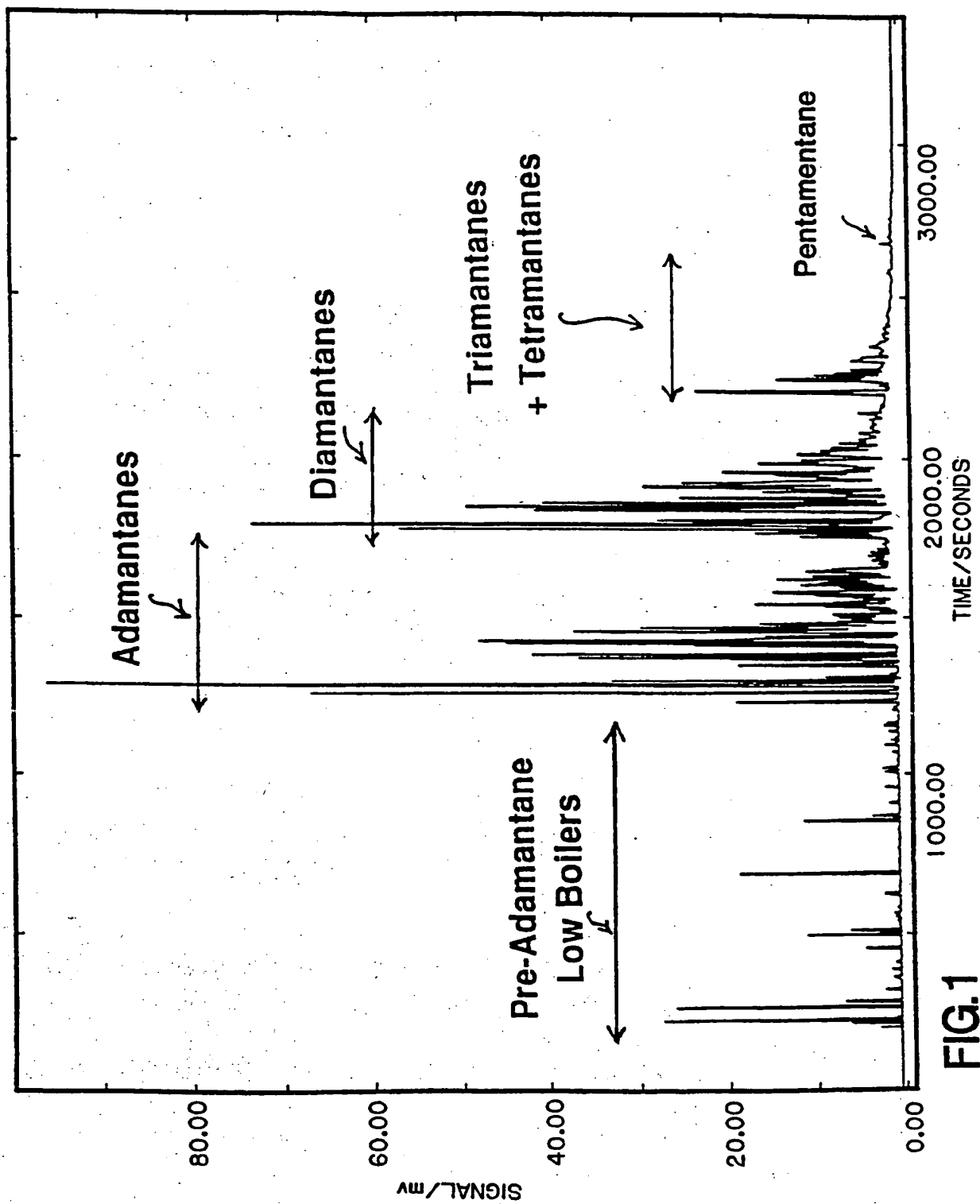
(k) distilling the liquid fractions recovered from steps (c) through (j) with reflux to recover substituted diamondoid compounds.

6. The method of claim 5 wherein said feed mixture contains less than about 25 weight percent of diamondoid compounds which are solid under ambient conditions.

7. The method of claim 5 wherein said feed mixture contains at least about 25 weight percent of diamondoid compounds and wherein said method further comprises at least one distillation step in the absence of reflux.

8. The method of claim 5 wherein said feed mixture contains at least about 25 weight percent of diamondoid compounds and wherein said method further comprises at least one filtration step at temperature less than or equal to ambient.

1/5



2/5

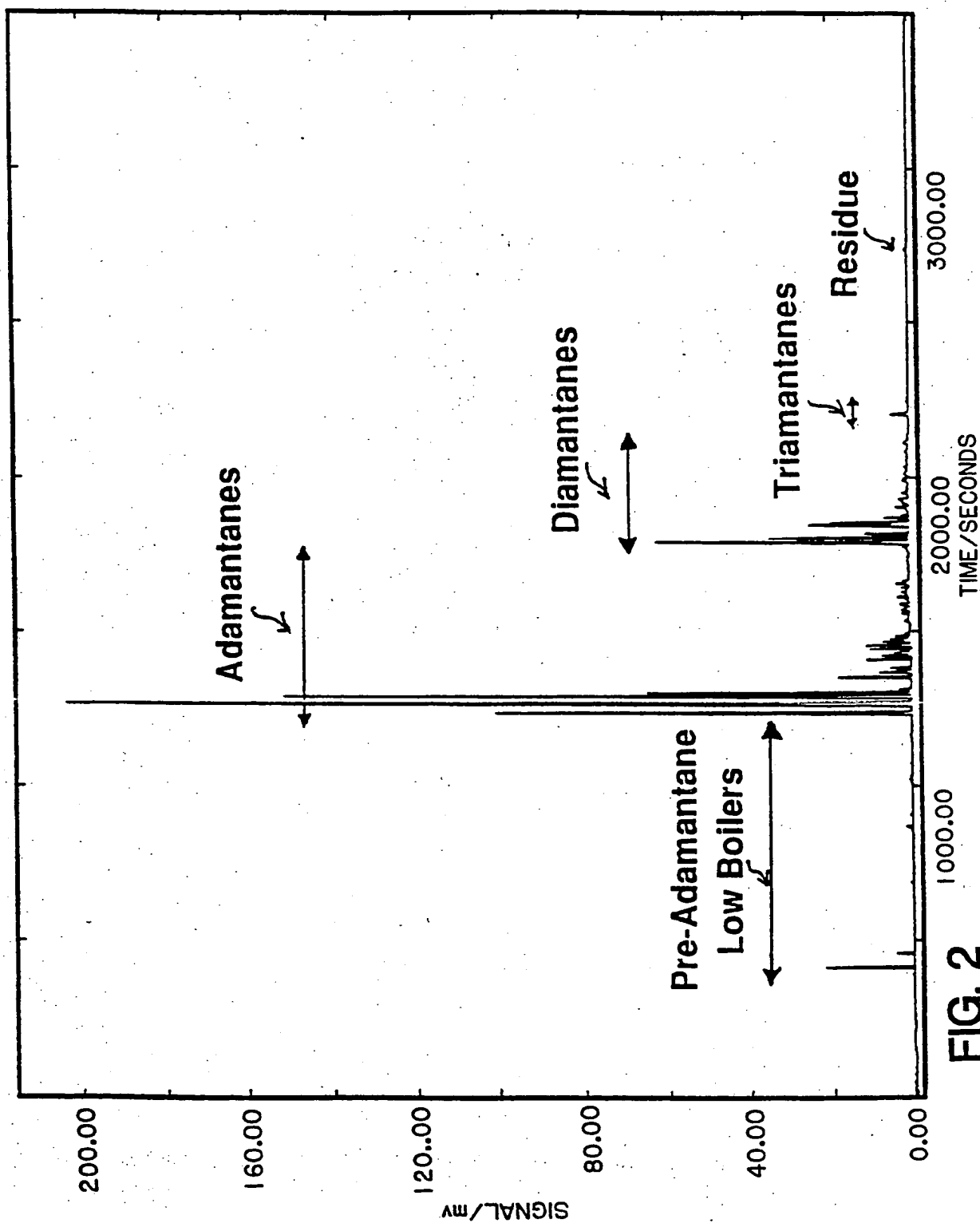


FIG. 2

3/5

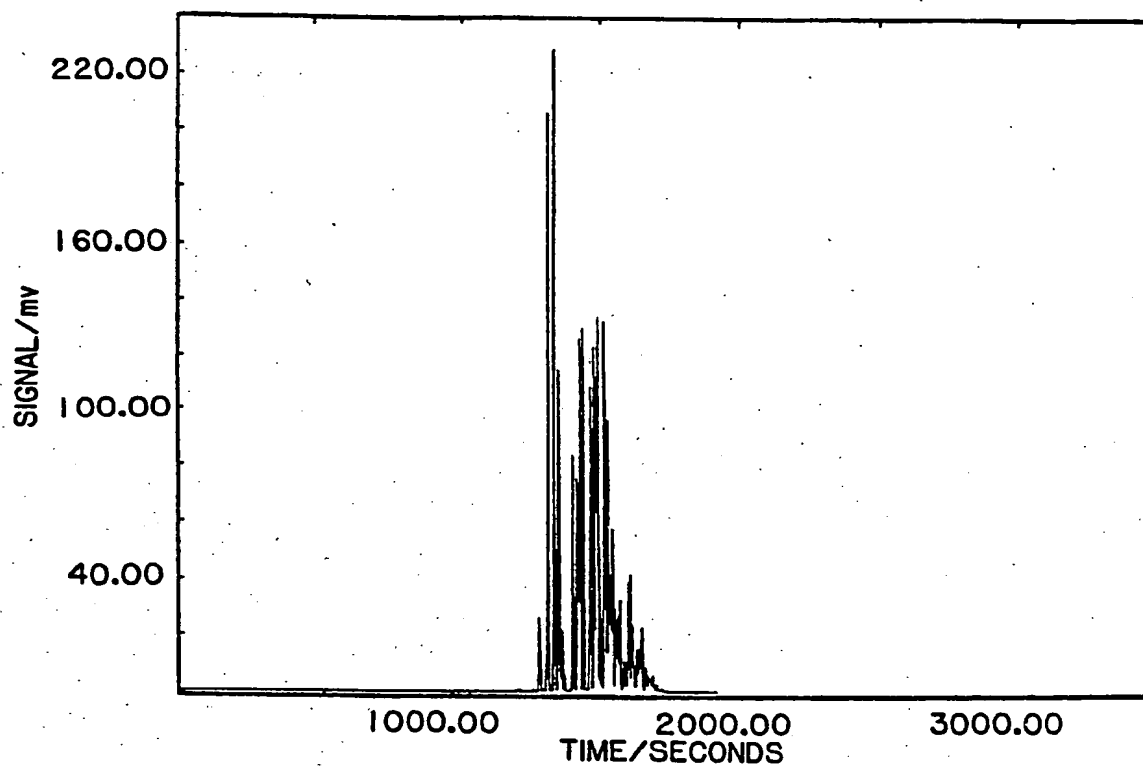


FIG. 3A

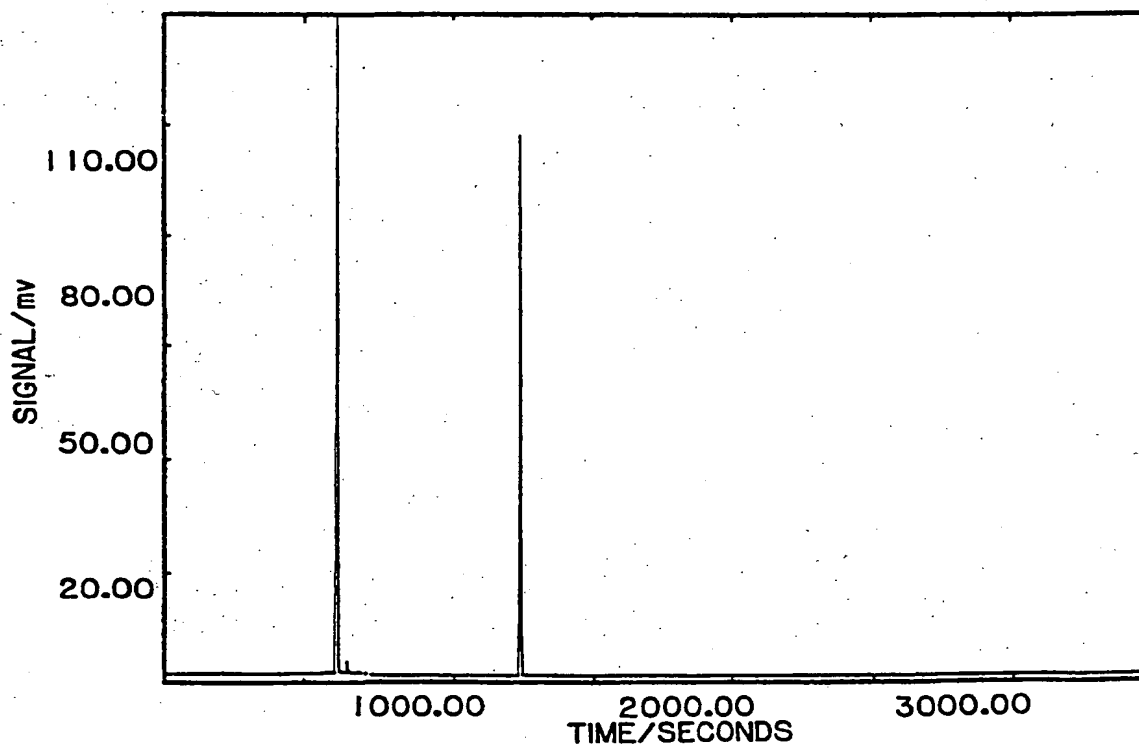


FIG. 3B

4/5

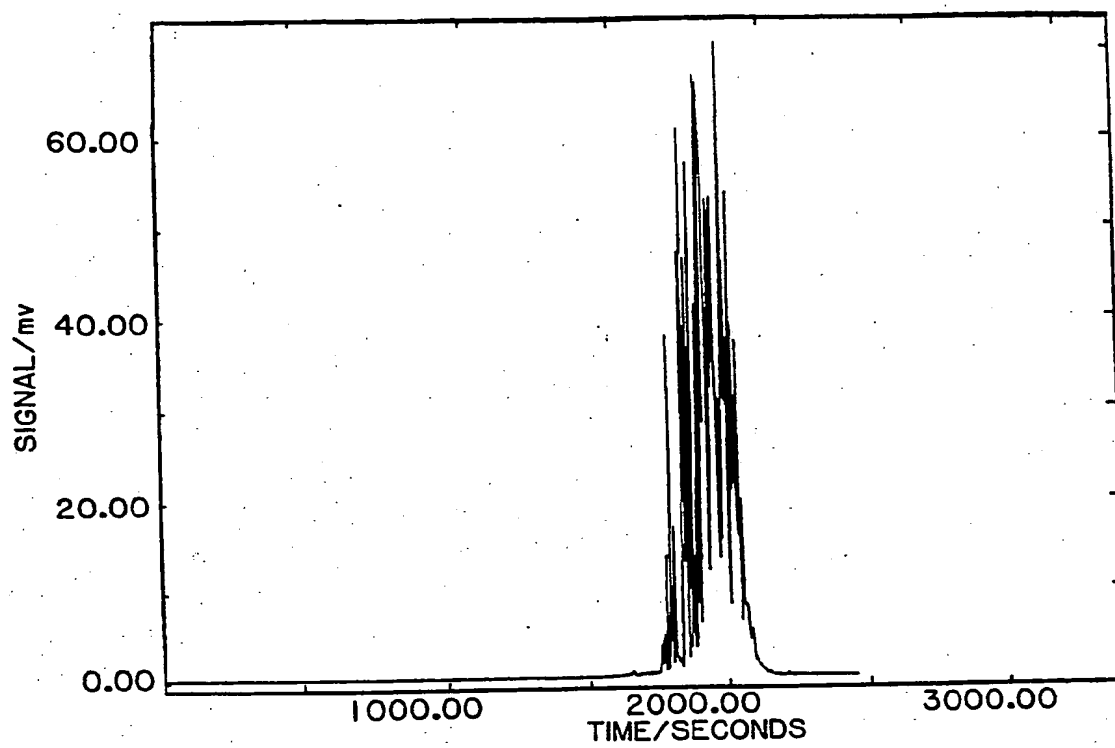


FIG. 4A

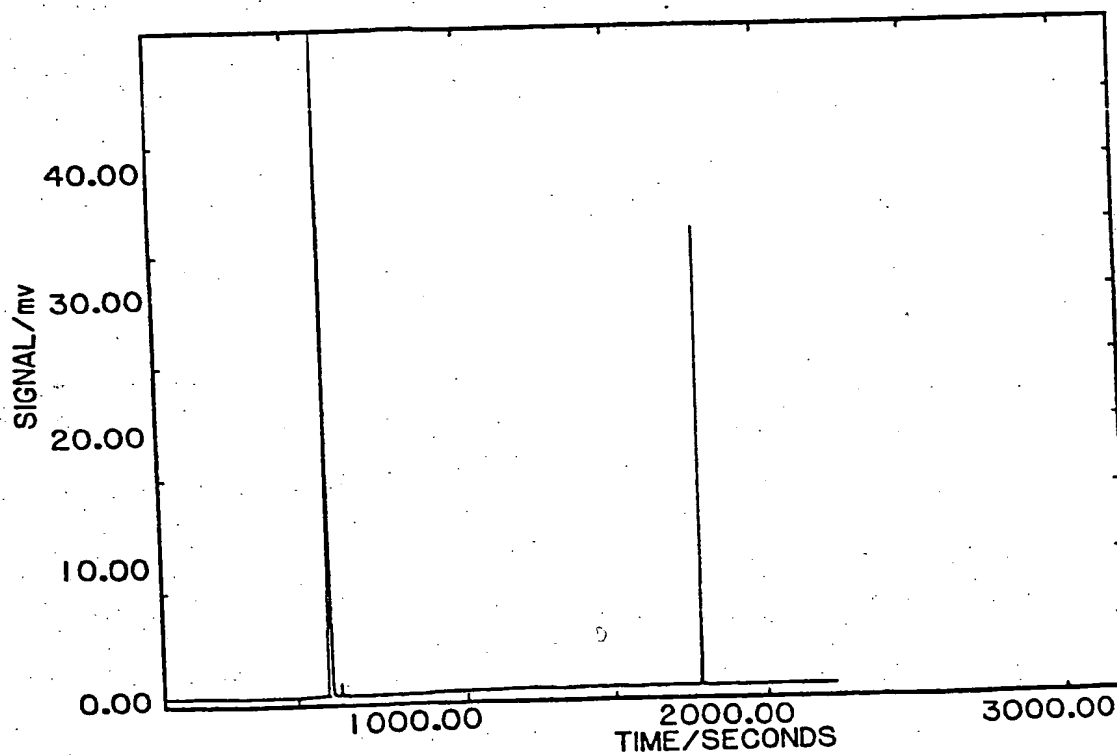
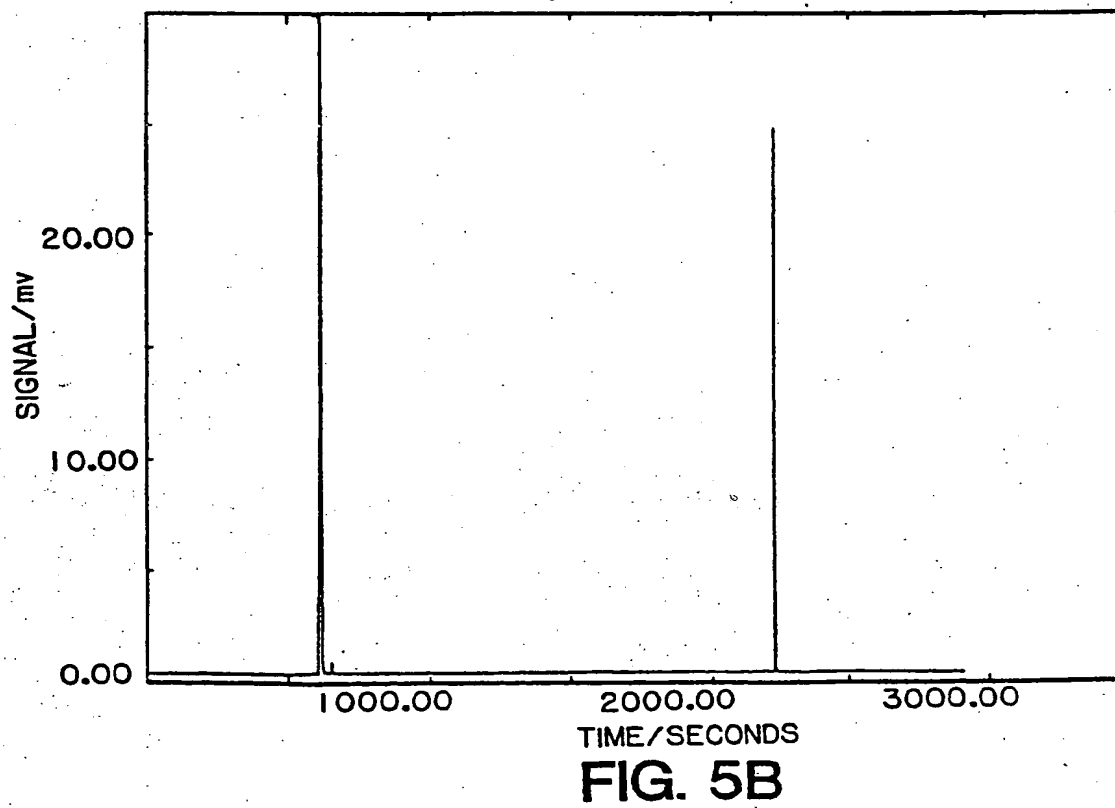
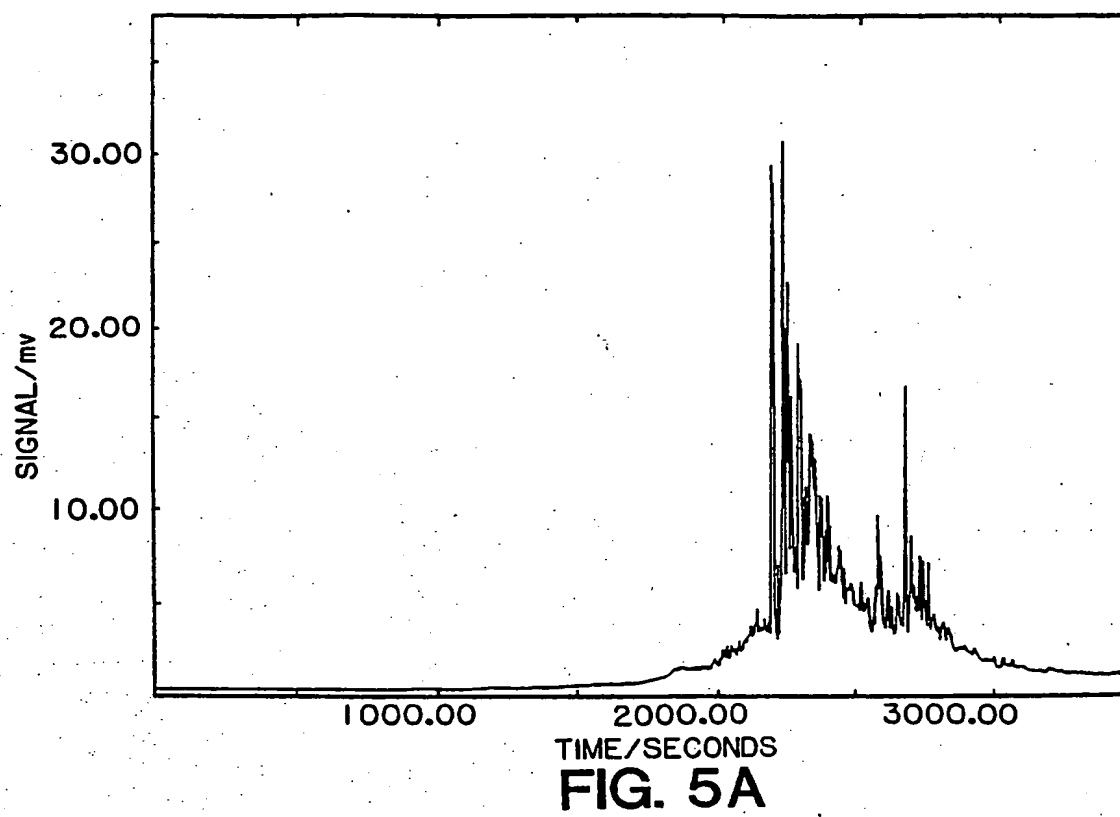


FIG. 4B

5/5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/09435

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C07C 7/04

US CL : 585/812, 815, 801

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/812, 815, 801

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,944,626 (HONNA ET AL.) 16 MARCH 1976, ALL PAGES	1-8
Y	A Text-book of Practical Organic Chemistry (Longmans, Green and Co.), published 1957, Arthur I. Vogel, pages 108-127.	1-8
Y	Aldrich Catalog, published by Aldrich Chemical Company, Milwaukee, Wisconsin, 1992, pages 1606-1615	1-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 SEPTEMBER 1994

Date of mailing of the international search report

3 NOV 1994

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

ASOK PAL

Telephone No. (703) 308-3809

THIS PAGE BLANK (USPTO)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 005953-156	FOR FURTHER ACTION		see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US 02/ 00504	International filing date (day/month/year) 17/01/2002	(Earliest) Priority Date (day/month/year) 19/01/2001	
Applicant CHEVRON USA, INC.			

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1

☐ None of the figures.

THIS PAGE BLANK (USPTO)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/00504

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C13/64 C08G61/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CA 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; → SHEN, MINGZUO ET AL: "Finite Td symmetry models for diamond: from adamantane to super-adamantane (C35H36)" retrieved from STN Database accession no. 116:40599 CA XP002201157 abstract & J. AM. CHEM. SOC. (1992), 114(2), 497-505 ,	1
X	→ WO 95 06019 A (MOBIL OIL CORP) 2 March 1995 (1995-03-02) see claim 5 (j) figure 1 -/-	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

5 June 2002

Date of mailing of the international search report

31/07/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Goetz, G

THIS PAGE BLANK (USPTO)

II INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/00504

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 410 092 A (SHEN DONG-MING) 25 April 1995 (1995-04-25) column 1, line 22-24 column 1, line 32-37 -----	1
X	US 5 019 660 A (CHAPMAN ORVILLE L ET AL) 28 May 1991 (1991-05-28) example 8 -----	1-85

THIS PAGE BLANK (5876)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 02/00504

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9506019	A	02-03-1995	US 5414189 A	09-05-1995
			AU 678853 B2	12-06-1997
			AU 7635494 A	21-03-1995
			EP 0715612 A1	12-06-1996
			JP 9501696 T	18-02-1997
			WO 9506019 A1	02-03-1995
US 5410092	A	25-04-1995	US 5298666 A	29-03-1994
US 5019660	A	28-05-1991	CA 2100654 A1	13-08-1992
			WO 9213909 A1	20-08-1992
			AU 661654 B2	03-08-1995
			EP 0571377 A1	01-12-1993
			JP 6504981 T	09-06-1994

THIS PAGE BLANK (USPTO)